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Application of Graphene Oxide- Magnetic Nanoparticle for Solid Phase Extraction of Trace Amounts of Cadmium Ions in Environmental Samples

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Abstract

In this work, Fe_3O_4-graphene oxide nanocomposite (GO-Fe_3O_4) was prepared as effective absorbent for magnetic solid phase extraction (MSPE) of trace quantities of cadmium ions in environmental water and rice samples using 1, 2-dihydroxy anthraquinone-3-sulphonic acid, sodium salt (Alizarin red S) and flame atomic absorption spectrometry (FAAS). The GO-Fe_3O_4 was characterized by scanning electron microscopy (SEM) and X-ray powder diffraction (XRD). Various parameters affecting GO-Fe_3O_4 MSPE of cadmium have been investigated. Under the optimized experimental conditions, the limit of detection (LOD) for Cd^{2+} in the range of 1-50 ngL^{-1} were 0.21 and the relative standard deviation (RSDs, c=50 ngL^{-1}, n=7) were 3.2 %. The developed GO-Fe_3O_4 MSPE-FAAS method has the advantages of rapidity, simplicity, good sensitivity, and it is suitable for the analysis of trace cadmium in samples with complex matrix.

Keywords: Graphene oxide; Fe_3O_4; nanocomposite; magnetic solid phase extraction; Alizarin red S; cadmium; rice; water sample

1.**Introduction**

Graphene has found as an exotic material of the 21st century [1], the honeycomb lattice is composed of two equivalent sub-lattices of carbon atoms. geraphene has led to a vast amount of research in recent years and attracted wide attention due to unique structural and physical properties. It has a huge theoretical specific surface area (2630 m^{2}g^{-1}) [2], suggesting a high sorption capacity. In the other hand for the immobilization of large amount of substance, and its π-electron rich system can possesses strong affinity for benzene ring [3, 4].

Geraphene oxide (GO) the oxidation product of graphene, consist of hexagonal carbon network containing hydroxyl, epoxide, carboxyl and carbonyl functional groups, is hydrophilic, negatively charged, and readily disperses in aqueous solution to form a stable suspension [5, 6]. These oxygen containing functional groups can bind withmetal ions, especially the multivalent metal ions, through both electrostatic and coordinate approaches, which makes GO an ideal adsorbent for

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metal ions Recently, the utilization of GO as asorbent for the removal of heavy metal ions from water has been reported [7,8]. However, the graphene oxide sheets were difficult to isolate completely from the dispersions even by high speed centrifugation because of the presence of miniscule sheets of graphene oxide. Furthermore, the procedure is quite trouble- some, tedious and offers in efficient retrieval of graphene. Introducing magnetic properties into graphene could combine the high adsorption capacity of the graphene and the separation convenience of the magnetic materials [9].

Recently, magnetic nanoparticles, mainly including Fe_3O_4 nanoparticles, appear as interesting advanced composite materials. It has received a great deal of attention because of the ease and simplicity in recovering adsorbent from the liquid phase [10, 11]. However, pure magnetic nanoparticles suffer from some inherent limitations as they tend to agglomerate, which may alter their magnetic properties in complex matrices [12, 13]. Moreover, these nanometer sized metal oxides are not target selective and are unsuitable for samples with complicated matrices [14]. Additionally, Fe_3O_4NPs are also known to have low toxicity, low cost and eco friendliness when serving as stabilizer [15]. To overcome such limitations creating an appropriate Fe_3O_4 nanocomposite is essential.

Alizarin red S (ARS) is a well-characterized organic chelating ligand for certain metal ions [16, 17]. It is reacts with metal ions to form an ionic chelates, which are not extractable into organic solvents. The presence of quinoid oxygen with two hydroxyl groups in the ARS structure makes it very suitable for the formation of stable complex with metal ions under controlled pH conditions. ARS has been immobilized onto various supports such as Amberlite XAD-2 resin [18], silica gel [19] and alumina [20] and is used for the separation and preconcentration of trace metals.

Urban areas produce large amounts of pollutants that accumulate on different surfaces such as streets and roofs. During rain events and snowmelt, these pollutants are transported into the storm sewer system, from where they either reach treatment facilities or directly discharge to receiving waters. Storm water contains large variety of pollutants e.g. heavy metals (lead, zinc, copper, cadmium, chromium and nickel), organic compounds, nutrients, solids, and deicing agents [21]. Among those heavy metal species, cadmium has been described as one of the most hazardous heavy metals in food and the environment due to its ability to induce severe alterations in various organs and tissues following either acute or chronic exposure [22]. Kidney, liver, lung and pancreas are the main organs of human for accumulation of cadmium. All soils and rocks, including coal and mineral fertilizers, contain some cadmium. Cadmium is an industrial waste or byproduct, which has a great environmental concern. Cadmium is used in many industrial processes, such as a constituent of easily fusible alloys, soft solder, electroplating and deoxidizer in nickel plating, engraving processes, electrodes for vapor lamps, photoelectric cells, and nickel cadmium storage batteries [23]. Although essential function of cadmium on human body is not clearly known, it may cause toxic effects even at very low doses. This toxicity could be due to a direct or an indirect interaction taking place between the metal and the biological system, as it could be the form of both extracellularly and intracellularly. Cadmium acts as inhibitor of sulphydryl enzymes and has an affinity for other ligands in cells such as hydroxyl, carboxyl, phosphatyl, cysteinyl and histidyl side chains of proteins [24]. In cancer studies, it has been reported that this metal is a mutagen in mammalian [25, 26] and at concentrations higher than the maximum permissible level, it may result in prostate, renal and lung cancers [27]. The FAO/WHO Joint Expert Committee on Food Additives recommended provisional maximum tolerable daily intake of Cd from all sources (food, air, and water) of 1.0–1.2 µg/kg mass of body [28]. Moreover, the national and international regulations on food quality are lowering the maximum permissible levels of toxic metals in human food; thus, the maximum permissible level of Cd in drinking water is 3.0 μgL^{-1} [29, 30]. Therefore determination of trace amounts of cadmium in environmental samples has a great importance.

The atomic absorption spectrometry is the most common technique used for the trace metals determination in different samples. There are some difficulties on determination trace quantities of some metals in environmental samples. Generally, the concentrations of some metal ions are lower than the detection limit of most instrumental techniques or metals usually exist in very complex matrix and matrixes generally have interferences on even the concentration of species under investigation is higher than the detection limit [31,32]. Because of these difficulties, a cleanup and preconcentration step is usually required to obtain more reliable data [33]. Thus, solid phase extraction (SPE) has become a preferred method for concentrating the analyte prior to its analysis by FAAS and other techniques. SPE has become to the forefront compared to other preconcentration and/or separation techniques, as it offers several advantages such as flexibility, higher enrichment factors, absence of emulsion, low cost, high speed and simplicity, safety with respect to hazardous samples and more importantly friendly to environment[34–36].

Recently, a new mode of SPE, based on using magnetic or magnetically modified adsorbents called magnetic solid phase extraction (MSPE) has been developed. MSPE technology exhibits excellent adsorption efficiency and rapid separation from the matrix by an external magnetic field, which makes separation process easier and faster without the need of additional centrifugation or filtration steps. MSPE can avoid the time consuming column passing operations encountered in SPE. Due to such advantages, MSPE has been widely used in many fields [37–40]

Therefore, the purpose of this work was to prepare graphene based magnetic nanoparticles (GO-Fe3O4) and develop a novel method of magnetic solid phase extraction (MSPE)-FAAS for the determination of traces amounts of cadmium ions from rice and environmental water samples.1, 2-dihydroxy anthraquinone-3-sulphonic acid, sodium salt (Alizarin red S) a chelating agent which forms stable complexes with different metals was used to extract Cd (II). Moreover, it possesses a benzene ring structure. Therefore, the Cd- ARS complex is considered to have formed a strong π-stacking interaction and hydrophobic interaction with graphene oxide when the adsorbent is dispersed in a sample solution. Experimental parameters affecting MSPE were studied in detail and the optimal experimental conditions were established. The developed method has been successfully applied for the determination of trace cadmium in rice and environmental water.

2.Experimental

Instrumentation

An Aurora flame atomic absorption spectrometer Al1200 (Canada) furnished with a Cd hollow cathode lamp and air–acetylene flame, was used for the analysis. The absorbance wavelength was set at 228.8 nm and the spectral band width at 0.7 nm. X-ray diffraction (XRD) measurements were carried out using a Bruker, D8-advance diffractometer with Cu Kα radiation (λ=1.541874Å) at a generator voltage of 40 KV and a generator current of 30mA.Infrared spectra were recorded using a Fourier transform infrared spectrometer (FT-IR, Perkin Elmer, Spectrum RX1) to identify the functional groups and chemical bonding of the coated materials. The morphologies of the nanocomposite were recorded on a S 360 Cambridge scanning electron microscope (SEM). A Metrohm744 digital pH-meter (Herisau, Switzerland) equipped with a combined glass electrodewas used for the pH measurements.

3. Reagents and solutions

A stock solution of cadmium (II) (1,000 mg L^{-1}) was prepared by dissolving an appropriate amount of Cd $(NO_3)_2.4H_2O$ and working standard solutions were obtained by appropriate step-wise dilution of the stock standard solutions. All stock and working standard solutions were stored in polypropylene (PP) bottles, with a leak proof screw cap, which were cleaned before use by soaking in 10 % nitric acid solution for at least 24 h and then rinsing thoroughly with double distilled water. Ferrous ammonium sulfate $[(NH_4)_2SO_4FeSO_4.6H_2O]$ and ammonium ferric sulfate $[NH_4Fe\ (SO_4)_2.12H_2O]$ P_2O_5, $K_2S_2O_8$, H_2O_2, $KMnO_4$, HCl, H_2SO_4, acids, and solvents were purchased from Merck Company (Darmstadt, Germany). Graphite powder were bought from Fluka.

Synthesis of graphene oxide

The graphite powder (10 g) was put into a 3-necked round-bottom flask containing an 80°C solution of concentrated H_2SO_4 (15 mL), $K_2S_2O_8$ (5 g), and P_2O_5 (5 g). The obtained dark blue mixture was thermally isolated and allowed to cool to room temperature over a period of 6 h. The mixture was then carefully diluted with distilled water, filtered, and washed with distilled wather until the pH of rinse water became neutral. The product was dried in air at ambient temperature over night. This preoxidized graphite was then subjected to oxidation by Hummers' method. The oxidized graphite powder (10 g) was put into cold (0 °C) concentrated H_2SO_4 (230 mL) then $KMnO_4$ (30 g) was added gradually with stirring and cooling in ice bath, so that the temperature of the mixture was not allowed to reach above 20 °C. The mixture was then stirred at 35 °C for 2 h, and distilled water (460 mL) was added. In 15 min, the reaction was terminated by the addition of a large amount of distilled water (1.4 L) and 30% H_2O_2 solution (25mL), after which the color of the mixture changed to bright yellow. The mixture was filtered and washed with 1:10 HCl solution (2.5 L) in order to remove metal ions and finally the product was air dried.

Synthesis of MGO

The preparation of iron oxide magnetic nanoparticle was performed by co precipitation of iron oxide nanoparticles on the surface of GO nanomaterials [41]. Typically, 1 g of dry GO was dispersed in 100 mL ultrapure water with ultrasonication to form stable suspension. Then, 5.8 g ferrous ammonium sulfate and 10.7 g ammonium ferric sulfate were dissolved in 100 mL ultrapure water to form mixed iron salt solution under oxygen free condition. Subsequently, 10 mL aqueous ammonia (wt. 25%) was rapidly added into the mixed solution to produce iron oxide nanoparticles, followed by slow addition of GO suspension with stirring. The reaction was continued for 45 min at 85°C with stirring for 45 min and then cooled to room temperature. Finally, the MGO solid was collectedby a magnet and washed with ultrapure water and anhydrous ethanol for three times, then it dried at 70°C for 12 h in vacuum oven.

Magnetic solid phase extraction procedure

The general procedure for the extraction of cadmium by GO-Fe_3O_4 MNPs was as follows: An aliquot of 400 μL of 6.0×10^{-3} mol L^{-1} ARS and then 30.0 mg of GO-Fe3O4 was added to a beaker containing 25 mL of an aqueous sample solution (pH=5.5) of Cd(II). The mixture was dispersed by ultrasonication for 2 min at room temperature, and then the adsorbent GO-Fe3O4 was isolated from the solution by placing a strong magnet at the bottom of the beaker and the aqueous phase was easily decanted by simply inverting the beaker. Desorption of target ions was performed by adding 1 mL of 1mol $L^{-1}HNO_3$ solution to sorbent. After shaking manually, the sorbent was separated by positioning the magnet to the outside of the tube and the concentration of cadmium in acidic aqueous phase was determined by FAAS.

Sample preparation

In order to demonstrate the applicability and reliability of the method for real world samples, method was applied to extraction of cadmium in rice and water samples. The rice were purchased from local supermarkets in Shiraz. At first, the samples were cleaned with double-distilled water and dried for 24 h at room temperature then ground into powder before digestion. After that 4 g of rice sample was transferred into beaker then 16.0 mL of HNO_3 1 mol L^{-1} was added and the vessel was heated on a hot plate at 95 °C for 2–3 h, until it dried. Then 3.0 mL of H_2O_2 (30%) were added and heated, untill a clear transparent solution was obtained. The sample was cooled to room temperature, filtered with filter paper transferred to a volumetric flask and reach to 100 mL with distilled water. pH of the samples was adjusted to 5.5 before them analyzed by described procedure .

Tap water and river water were filtered through a Millipore 0.45 mm pore size to remove suspended solids. River water sample was collected from Sheshpir river and tap water sample was collected from Golestan town of Shiraz. Each sample after treatment were used to extraction of cadmium under optimal conditions of the method.

4. Results and discussions

Characterization of the adsorbent

X-ray diffraction (XRD) measurements were employed to investigate the phase and structure of the synthesized GO and GO-Fe_3O_4. As shown in Fig. 1, the XRD pattern of the prepared GO (Fig. 1a) shows a broad peak at $2\theta = 10.35^\circ$. The 0 0 2 reflection is very broad suggesting that the materials are very poorly ordered along the stacking direction. This is an indication that the material comprises largely free GO sheets. From Fig. 1b, except for the diffraction peak at $2\theta = 10.35^\circ$resulting fromGO, all the new significant diffraction peaks of the GO/Fe_3O_4 which are matched well with the data from the JCPDS card (19-0629) forFe_3O_4(the diffraction angles at 2θ): 18.1◦, 30.15°, 35.6°, 43.25°, 53.7°, 57.1° and 62.85°can be assigned to (1 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1),and (4 4 0) of the pure cubic spinel crystal structure of Fe_3O_4.

Figure 2 portrays the SEM images of graphene oxide and the GO-Fe_3O_4 nanocomposite. graphene has a smooth surface with a distinctive layered appearance (Fig.2a). As shown in Fig.2b, the iron oxide nanoparticles were well distributed on GO sheets, which were nearly flat and had a big area up to several square micrometers. Some nanoparticles were slightly aggregated due to the loading degree close to saturation.

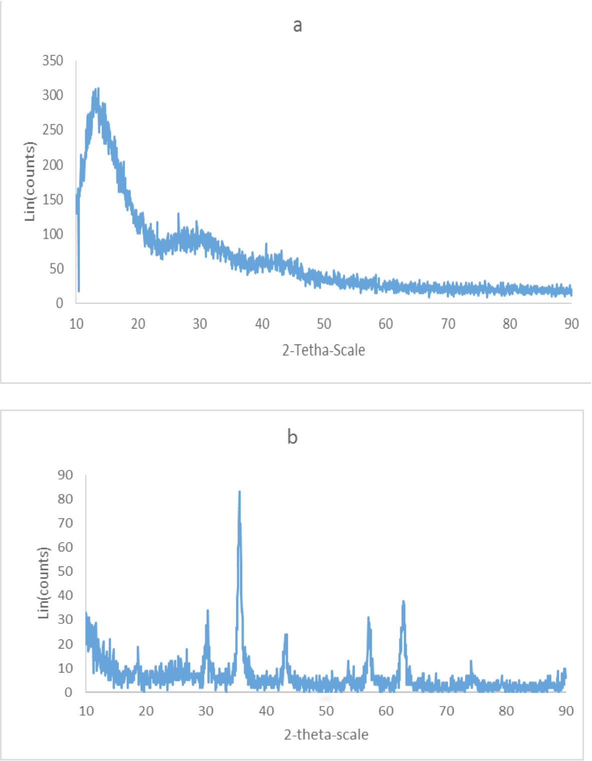

Fig. 1. X-ray diffraction pattern of GO (a) and GO-Fe_3O_4 (b)

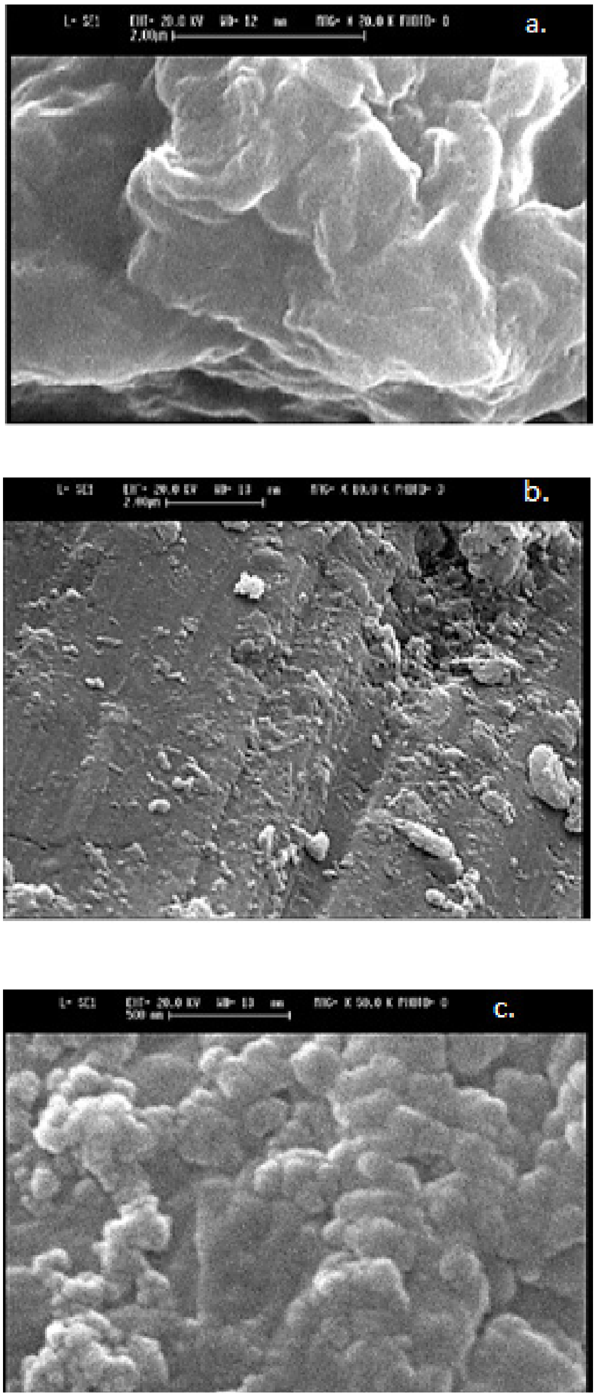

Fig. 2. Scanning electron micrographs of (a) graphene oxide and (b, c) Go-Fe3O4 nanocomposite at low and high magnification

Optimization of magnetic solid phase extraction procedure

Effect of pH

Since the pH of the sample solution is an important factor in the solid phase extraction of the metal ions, the effect of pH on the recovery of analytes in the pH range of 3.0–8.0 was investigated. Based on the obtained results, the extraction recovery of cadmium (II), increased as the pH in the aqueous solution was increased up to 5.5 and then after that, the extraction recovery starts to decrease. Thus, pH 5.5 seems to be a proper choice for both complexation and extraction. The decrease in recoveries at low pH is probably attributed to the competition of hydrogen ions with the analytes towards the complexation with ARS, whereas the decrease in recoveries at high pH may be probably due to the formation of hydroxide of the metal ions.

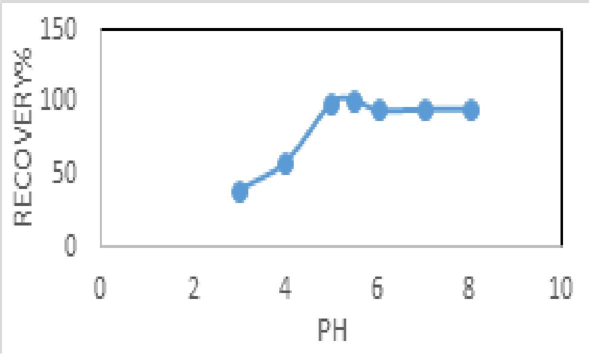

Fig 3. Influence of pH on the recovery of Cd(II). Conditions: Amount of metal ions: 50μgL^{-1} Cd(II), 8×10^{-6}mol L^{-1}of ARS, amount of sorbent: 30 mg, eluent (HNO_3) concentration: 1.0 mol L^{-1}, eluent volume: 1.0 mL

Effects of ARS concentration

Concentration of the ligand is also an important factor for the quantitative retentions of metal ions in solid phase extraction techniques. In order to investigate the optimum concentration of ARS on the quantitative recoveries of the cadmium ions on GO-Fe_3O_4, the study was examined by varying the concentration of ARS from 6.0×10^{-4} – 6.0×10^{-7}mol L^{-1}. As it can be seen, maximum recovery was obtained at a concentration of 6.0×10^{-6} mol L^{-1}of the ligand and after that, recoveries approximately stays constant.

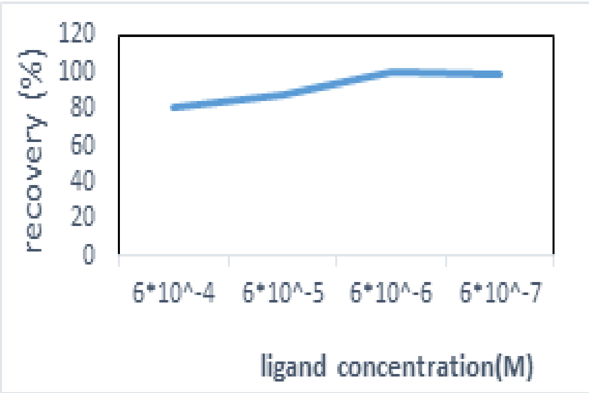

Fig. 4. Influence of concentration of ARS on the recovery of Cd (II). Conditions: Amount of metal ions: 50μgL^{-1} Cd (II), amount of sorbent: 30 mg, eluent (HNO_3) concentration: 1.0 mol L^{-1}, eluent volume: 1.0 mL

Because of some other ions that could be present in real samples and probably react with ARS, a concentration of 6.0×10^{-6} mol L^{-1} was used in experiments. The extraction recovery was not affected by the addition of ligand excess. Therefore, the concentration of 6.0×10^{-6} mol L^{-1} was chosen for subsequent experiments.

Effect of equilibrium time and amount of sorbent

In order to investigate the effect of equilibrium time on the extraction recovery, The influence of elution time varying from 1 to 15 min on the recovery of the cadmium(II) was also investigated. It was found that the cadmium (II) could be quantitatively recovered when the elution time was above 1 min, which indicates that the prepared GO-Fe_3O_4 has fast elution kinetics for cadmium (II). For the optimization of the amount of adsorbent, 10–60 mg of the GO-Fe3O4 was tested. Results showed that by increasing amounts of the GO-Fe_3O_4 the extraction efficiency increased due to increase in the surface area and accessible sites for adsorption of the analytes, Quantitative extraction of the cadmium ions was achieved using only 30mg of the GO-Fe_3O_4. At higher amounts of the adsorbent, the extraction efficiency was almost constant.

Choice of eluent type, concentration and volume

To ensure the complete elution of the target analyte from the adsorbent, the type, volume, and concentration of the eluent should be studied. A series of selected eluent solutions such as HNO_3, HCl, ethanol and methanol in different concentrations were used to elute cadmium ions from the adsorbent surface. As shown in Table 1, it was eventually found that HNO_3 (1.0 mol L^{-1}) provided effective elution of cadmium ions from the adsorbent surface. In order to choose the proper volume of eluent, the retained Cd ions were eluted with different volumes (0.5–3mL) of 1.0 mol L^{-1} HNO_3. The elution was found to be quantitative using 1 mL of 1.0 mol L^{-1} HNO_3. Hence, subsequent elution experiments were carried out with 1 mL of 1.0 mol L^{-1} HNO_3.

Table 1. Effect of eluting solution (1 mL) on the recovery of Cd (II)

Recovery (%)	Eluent
99.8	1 mol L^{-1} HNO_3
93.2	2 mol L^{-1} HNO_3
87.9	1 mol L^{-1}HCl
81.6	2 mol L^{-1}HCl
2.1	etanol
26.4	1mol L^{-1} HNO_3 in ethanol
3.7	metanol
59.5	1mol L^{-1} HNO_3 in methanol

Effect of sedimentation time

In this study, the adsorbent could be separated rapidly from the sample solution using an external magnetic field instead of filtration or centrifugation, due to the super paramagnetism of GO-Fe_3O_4. Effect of sedimentation time on the recovery of Cd ions was investigated and the experimental results are shown in Fig 5. It can be seen that the GO-Fe_3O_4 could be completely sedimented with quantitative recoveries of target Cd ions when the sedimentation time was 1 min. In subsequent experiments, a sedimentation time of 1 min was employed.

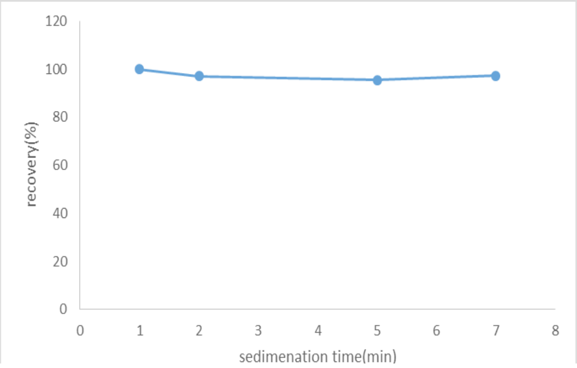

Fig. 4 .effect of sedimentation time

Effect of sample volume

The break through volume is the maximum sample volume without significant loss of analytes. The break through volume depends on the nature of the sorbent, nature and concentration of the analyte and mass of the sorbent. In order to obtain a higher enrichment factor, a larger sample volume is required. To investigate the effect of the sample volume on the recoveries of the cadmium (II), the sample solutions of 10, 25, 50, 100 and 200 mL containing 2.5 μg of cadmium (II) were prepared and subjected to the general procedure, respectively. It is found that the recovery of cadmium (II) was quantitative when the sample volume was in the range of 10–50 mL, and then slightly decreased with further increase of sample volume to 200 ml. In subsequent experiment, 50 mL sample volume was used, and an enrichment factor of 50 was obtained by applying 1 mL of 1 mol L^{-1} HNO_3 as the elution solution.

Effect of Interfering Ions

ARS is a non-selective chelating agent and favorably reacts with many metal ions. The effects of various foreign ions on the recovery of cadmium and lead were examined. In an ambience of competitive ions were added to the test solution containing 50 ng $mL^{-1}$of cadmium and the signals were compared to that of a solution containing only Cd(II). The results showed in Table2, there isn't any serious interfere in this method the tolerance limits were taken for a maximum error of 5%. As can be seen, the tested cations, at concentration levels higher than those usually present in real samples, were not found to impair the effectiveness of the developed method.The recoveries of some other ions were also investigated according to the developed procedure.

Table 2. Effects of coexisting ions on the determination of Cd^{2+} (50 ng mL^{-1})

Ions	Ratio of Interfering Ions
NO_3^-, SO_4^{2-}, CO_3^-, Br^-, Cl^-, CH_3COO^-, K^+, Na^+, Ca^{2+}, Mg^{2+}	1000
Pb^{2+}, Zn^{2+}	100
Fe^{2+}, Fe^{3+}, Ni^{2+}	40
Cu^{2+}, Al^{3+}, Cr^{3+}	20

Sorption capacity

Adsorption capacity is an important factor to evaluate the performance of sorbent. The sorption capacity of the GO-Fe_3O_4 for cadmium was calculated by adding 100 mg of the sorbent into 200 mL of the solution containing 10 mgL^{-1} of cadmium (II) at pH 5.5. After shaking it for 2h, MGO adsorbent was separated from aqueous solution by a permanent magnet, 10 mL of the supernant solution was diluted to 50 mL and the analytes were determined by flame atomic absorption spectrometry. The sorption capacity of the sorbent was found to be 11.1 mg g^{-1} for cadmium, respectively. Analytical performance

Under optimomd conditions, a calibration curve for Cd (II) was obtained by preconcentration a series of Cd (II) standards according to the recommended procedure. The curve was linear from 1 to 50 ng mL^{-1} for Cd (II). The calibration equation is $A = 0.002\ C + 0.0143$ with a good correlation coefficient of 0.999 where A is the atomic absorbance of Cd(II), obtained by peak height, in the eluent at 228.8 nm and C is its concentration in the sample solution (ng mL^{-1}). The limit of detection, defined as LOD =3 Sb/m, where LOD, Sb and m are the limit of detection, standard deviation of the blank and the slope of the calibration graph, respectively, was found to be 0.21 ng mL^{-1}. The relative standard deviation (RSD) for ten replicate measurements of 50.0 ng mL^{-1} of Cd (II) was 3.2 %. The results indicated that the developed method can be used as a simple and efficient extraction and pre concentration technique for trace cadmium in water samples prior to FAAS analysis and the graphene based magnetic nanocomposite may have a great application potential for the preconcentration of cadmium ions in different samples.

Application of the method

The developed method was used for the determination of cadmium in several environmental water and rice samples. The results, along with the recovery for the spiked samples, are given in Table 3. The recoveries for the addition of different concentrations of cadmium to environmental water and rice samples were in the range of 95.0–103.5 %. It can be concluded that the developed method is accurate and free of systematic errors.

Table 3 Analytical results of Cd determination in certified reference materials and spiked real samples with the MSPE-FAAS method (n=3)

Sample	Add Cd^{2+} µg L^{-1}	Found Cd^{2+} µg L^{-1}	Recovery %
Tap water	-	N.D	-
	10	9.8	98
River water	-	N.D	-
	10	10.06	100.6
1121 rice (foreign rice)	-	1.35	-
	10	10.85	95
Camfirooz rice(Iranian rice)	-	N.D	-
	10	10.35	103.5

Table 4. Comparison of the developed method with some recent studies for preconcentration of trace cadmium using solid phase extraction

Adsorbent	PF[a]	RSD (%)	LOD[b] (ng mL^{-1})	Linearlyc (ng mL^{-1})	Reference
MWCNTs	50	2.06	0.15	0.5-50	41
MWNTs (FAAS)	40	1.42	0.43	5-120	42
MWNTs (FAAS)	50[d]	3.20	0.30	up to 60	43
hromosorb101(FAAS)	31	2.50	0.37	0.02-2 [e]	44
Alumina nanoparticles (FAAS)	75[d]		0.14	0.4-20	45
Sulfur (FAAS)	250	4.70	0.20	1-20	46
Dipyridyl functionalized graphene(FAAS)	410	1.60	0.19	-	47
Duolite XAD-761 (FAAS)	200[d]	3.20	0.38	1.26-22	48
This work	50	3.20	0.21	1-50	-

a. Preconcentration factor: ratio of the highest sample volume and the lowest eluent volume
b. Limit of detection (μgL^{-1})
c. Relative standard deviation
d. Enrichment factor
e. mg L^{-1}

Comparison of analytical performance data with literatures

Comparison of this method with other SPE extraction methods used for preconcentration and FAAS determination of cadmium ions from various real samples signifies that the presented method has some improvements compared with earlier reported methods with significant merits (Table4). The presented magnetic solid phase extraction method has low limit of detection (0.21 μgL^{-1}), high preconcentration factor, wide linear range (1 –50), good repeatability (RSD %). All these results indicate MSPE that combined with FAAS is a very simple and sensitive method for the preconcentration and determination of cadmium ions in water and rice samples

Table 4 Comparison of the developed method with some recent studies for preconcentration of trace cadmium using solid phase extraction

5.Conclusions

In the present study, a graphene oxide-based Fe_3O_4 magnetic nanoparticles was synthesized and for the first time used as an effective adsorbent for the preconcentration of cadmium in water and rice samples. The method takes the advantages of both graphene adsorption and magnetic phase separation from the sample solution at the same time. The magnetic separation greatly improved the phase separations while avoided the time consuming column passing or filtration operations encountered in SPE. This method gives good accuracy, low limit of detection, high preconcentration factor, good precision and rapid adsorption rates for the target analyte. This method was successfully applied for determination of cadmium at low concentrations in real samples. In this method sample preparation time was minimized by the fact that no centrifugation is required for phase separation and collection

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